STANDARD OPERATING PROCEDURE

FOR

ROUTINE OPERATION OF THE THERMO ENVIRONMENTAL MODEL 43S SO_2 ANALYZER IN CRPAQS

STI-999214

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1. EQUIPMENT DESCRIPTION

The Thermo Environmental Model 43S pulsed fluorescence SO_2 analyzer will be used for the determination of low levels of sulfur dioxide.

1.1 THERMO ENVIRONMENTAL MODEL 43S PULSED FLUORESCENCE SO_2 ANALYZER

The Model 43S operating principle is based on measuring the emitted fluorescence of SO_2 produced by the gas's absorption of UV radiation. Pulsating UV light is focused through a narrow band-pass filter mirror allowing only light wavelengths of 1,900 to 2,300 angstrom units (A) to pass into the fluorescent chamber. SO_2 absorbs light in this region without any quenching by air or most other molecules found in polluted air. The SO_2 molecules are excited by UV light and emit a characteristic decay radiation. A second filter allows only this decay radiation to contact a photomultiplier tube (PMT). Electronic signal processing transfers the light energy impinging on the PMT into a voltage which is directly analyzed. This pulsed fluorescence principle of operation was accepted by EPA under equivalency specifications defined in the February 18, 1975, Federal Register, Volume 40, No. 33 (ESQA-0486-060).

The controls and indicators on the front of the Model 43S analyzer (from left to right) are: power toggle switch, SAMPLE FLOW rotameter, time constant, range and span test push buttons, SPAN potentiometer, and ZERO potentiometer. The connections and controls on the rear panel of the analyzer are: recorder output, contact closures for remote activation and data acquisition, tubing ports for EXHAUST and SAMPLE, fuse, filter, and power cord. The LED display indicates the concentration reading of input gases or sample air. Output voltages are used as the true indicator of concentration. Refer to the instrument manual for graphic representation of the controls and indicators.

The system schematic is also shown in the instrument manual.

1.2 ENVIRONICS MODEL 9100 DYNAMIC MULTI-GAS CALIBRATION SYSTEM

The Model 9100 multi-gas calibration system will be used at the continuous air monitoring station to perform zero, span, and precision checks, and multi-point calibrations on the SO2 analyzer. Instructions for use of the Model 9100 are found in that standard operating procedures manual.

1.3 DATA ACQUISITION SYSTEM

A data acquisition system (DAS) provided by Sonoma Technology, Inc. will be used to record the SO2 concentrations at the site. The SO2 analyzer will be connected to the DAS by using the analog output on the analyzer.

2. SOPS FOR THE THERMO ENVIRONMENTAL MODEL 43S SO_2 ANALYZER

2.1 GENERAL O&M METHODS

The Field Technician will check the analyzer twice a week and complete the SO2 service log during each check to verify the correct operation of the analyzer.

Copies of all the service logs and instrument and station logbook pages will be submitted to the Data Manager at the end of each week.

2.2 WEEKLY CONTROL PARAMETER CHECKS FOR THE THERMO ENVIRONMENTAL MODEL 43S SO_2 ANALYZER

Control parameter checks, described below, will be performed on the analyzer prior to multi-point calibrations; performance audits; and manual zero, span, and precision checks:

1. **Date, Time**--Record date and time of visit on the chart and SO_2 Service Log.
2. **Range Setting**--The full-scale for Range should be set at 200 ppb. If this range is not correct, change it accordingly, note in station and analyzer logbook and the service log for the Thermo Environmental Model 43S SO_2 analyzer. Any data recorded in other than the 0.0- to 200.0 ppb range must be clearly identified.
3. **Flow**--Observe the sample flow on the rotameter and record the unadjusted flow. A flow rate of approximately 0.5 LPM (+/- 0.1 LPM) is acceptable. If the flow is not at specification, corrective action must be taken. Contact Beth Wittig and Earle Wright for procedures. Note in Station Logbook. Enter initial and corrected flow on the Service Log for the Thermo Environmental Model 43S SO_2 analyzer.
4. **Vacuum**--Observe the pressure gauge (interior panel) and record inches of mercury (Hg). Vacuum should be between -10 and -25 inches Hg. If not at specification, contact Beth Wittig and Earle Wright for procedures. Note initial and corrected vacuum pressure (if adjusted) in Station Logbook and Service Log for the Thermo Environmental Model 43S SO_2 analyzer.
5. **Time Constant**—The time constant button has two positions: in and out. The "OUT" position provides a slower instrument response, but a smoother analog output. The "IN" position provides a faster response and a more sensitive analog output. For this project the button will remain IN. If the setting is not correct, change it accordingly, note in Station Logbook and Service Log for the Thermo Environmental Model 43S SO_2 analyzer.
6. **Zero Setting**--The zero setting is determined during the calibration of the instrument. This should not be adjusted unless the data has been bracketed by performing and unadjusted calibration. Record the potentiometer setting on the service log. If this setting has changed since the last time it was recorded, notify Beth Wittig as soon as possible.

7. **Span Setting**--The span setting is also determined during the calibration of the instrument. This should not be adjusted unless the data has been bracketed by performing and unadjusted calibration. Record the potentiometer setting on the service log. If this setting has changed since the last time it was recorded, notify Beth Wittig as soon as possible.
8. **Lamp Voltage**--The lamp voltage reading is the amount of voltage being supplied to the UV flash lamp. Typical range is between 800 and 1,200 volts with the voltage slowly increasing from 800 volts as the lamp ages. If the voltage is over 1200, contact Beth Wittig and Earle Wright as soon as possible.
9. **Inlet Filter**--The inlet filter should be checked during each site visit and changed if any dirt or moisture is present on the element. The initial change schedule will be weekly and will be modified by the Project Manager as needed.
10. **Operator Initials**--Initials of the operator who performed the service checks.
11. **Data review**--Check the DAS record since the last visit to detect signs of monitoring system malfunctions. Typical malfunctions that may indicate system problems are:
    a. A straight trace for several hours (other than minimum detectable),
    b. Excess noise,
    c. Periods where the trace drops below the zero baseline.
12. **Calibration Tank Pressure** -- Record the cylinder (primary) and output pressure (secondary) pressures to track the usage and ensure the output stays constant. If the cylinder pressure drops below 200 psi, contact Beth Wittig about replacing it. The output pressure should be set for 29 psi. If the pressure is not within +/- 3 psi, adjust the output, not the change in the station logbook, and contact Beth Wittig.

3. ZERO/SPAN/PRECISION CHECKS USING THE ENVIRONICS MODEL 9100 MULTIGAS CALIBRATOR

Zero and 40 ppb span checks will be automatically initiated nightly by DAS. During the nightly zero/span check, the calibration gases are sent to the instrument via the roof inlet. These checks will also be performed before and after any adjusted calibration.

On a weekly basis, a zero/span calibration check will be performed by sending calibration gases directly to the instrument, bypassing the roof inlet. Comparing the results from this procedure to those of the nightly zero/spans provides an indication of the sample line integrity. To manually initiate the zero/span sequence, select the SO2 Zero-Span.Cal script on the DAS. Double click on the script and the DAS will automatically control the Environics Model 9100 calibrator to perform a zero and span check on the SO2 analyzer. This task is to be completed on Tuesdays at the Bakersfield site as SO2 Task 2.

4. CALIBRATION PROCEDURES--ADJUSTED/UNADJUSTED

The outline and figures presented here describe procedures to be followed during adjusted and unadjusted calibrations of SO2 analyzers. The Field Technician should record all results in the SO2 analyzer log book (see Figure 3-1 for an example of a calibration log book entry). All calibration activities should also be recorded in the Site Logbook. The following equipment and reagents are needed:

1. Environics Model 9100 multi-gas calibration system with NIST-traceable flow rates;
2. NIST SO_2 gas cylinder or NIST permeation device [Note: Gas cylinder must have had NIST-traceable certification (EPA Protocol II) within the previous 18 months];
3. Zero air system;
4. DVM (optional); and
5. Calculator for regression analysis.

4.1 CALIBRATION TECHNIQUES DESCRIPTION

1. **Environics Model 9100 Multi-gas Calibration System**--The **Environics** Model 9100 calibrator is used as a permanent in-station calibration system. Whenever this calibrator is used, there are no set-up requirements other than to ensure that all parts of the system are operational and within specification. Whenever a portable calibrator is brought in or upon initiation of the in-station unit, the following preparations must be performed:

   a. **Pneumatic Connections**--Connect the manifold output from the Model 9100 to the SAMPLE port of the analyzer being calibrated. Be sure to vent excess flow not required by the analyzer.

   b. **Gas Cylinder, Zero Air, and Regulator Preparation**--Prior to attaching calibration gas cylinders to the system, regulators and accompanying lines must be flushed free of contaminants. The following procedures are to be used:

      (1) Connect a stainless-steel regulator to the span gas cylinder.

      (2) Close the delivery valve of the regulator.

Figure 3-1
SO_2 CALIBRATION REPORT

Project :		Site:		Date:	18-Apr-00
Tech:	EWW		Begin:	1:30 PM	End: 3:30 PM

STATION SO_2 ANALYZER

Make:	TECO	Range:	0 - 500 PPB	Settings	Before / After
Model:	43C	Filter:	YES	Span Setting.:	2.3 / 2.6
SN#:	59868-	Vacuu	22 In Hg	Zero Setting:	5.0 / 5.1

	324	m:				
		Flow Rate:	0.465 LPM	Lamp Voltage:	960	960

CALIBRATION EQUIPMENT

Calibrator		Cal. Gas Cylinder			MFC Calibrations	
					Gas	Air
Make:	Environics	ID #:	CC82948			
Model:	9100	Conc.:	48.80	ppm	Slope:	1.0022 0.0010358
SN#:	010386 (San Joiaquin Valleywide)	Cert. Date:	06-Mar-98		Inter:	0.3204 0.0575048

SO_2 CALIBRATION

	Calibrator			DAS				
Cal Point	Gas Display	Air Display	(x) SO_2 PPB	(y) SO_2 PPB	SO_2 mV	SO_2 Chart %	Error PPB	Error %
Zero	0.0	8.00	0	1			1	NA
1	9.0	8.00	55	58			3	5.5
2	24.0	8.00	150	153			3	2.0
3	34.8	8.00	218	221			3	1.4
4	50.0	8.00	313	318			5	1.6
5	66.0	8.00	414	420			6	1.4
	Mean Absolute Error:						3.5	2.4

			DAS
FAIL POINT:	Slope = > or <1 +/-0.15	Slope (m):	1.0405
	Inter = > or <+/-3% FS	Inter (b):	16.4168
	Corr. = <0.9950	r^2:	0.999143

Comment: Quarterly calibration.

			DAS	Chart
VALIDATED BY:	_____	Pass/Fail:	Pass	Pass

(3) Open the cylinder valve slowly until the cylinder pressure reads 500 to 1,000 psig, then close the cylinder valve.

(4) Open the delivery valve of the regulator and vent the gas from the regulator (do not allow the pressure to reach 0 psig).

(5) When the system has been flushed by three repetitions of opening and closing the main valve, the main valve should be left open and the delivery valve closed so that the system is leak-tight. Check the system for leaks using a suitable detergent solution.

(6) Connect a 1/4-inch FEP Teflon® line from the regulator to the calibrator bulkhead fitting marked port 2 – 5, as directed by the calibrator SOP. Any ports can be used if the SO_2 analyzer is the only monitor in the station requiring gas mixtures from the Model 9100. Adjust the regulator output pressure to 35 psig.

(7) Do not remove regulator from the cylinder or allow it to attain ambient pressure until all gas in the cylinder is expended down to 100 psig; do not use if gas pressure falls below 100 psig.

(8) Connect the output from the zero air system to the ZERO AIR port on the rear bulkhead panel of the Model 9100. Turn on the zero air system.

2. **Thermo Environmental Model 43S SO_2 Analyzer**--

a. Turn analyzer ON. Allow at least 24 hours for equilibration.

b. RANGE should be set to 200 ppb.

4.2 ADJUSTED CALIBRATION PROCEDURE

A sample line integrity check (SLIC) is to be performed following the initial installation, and quarterly prior to each calibration. The test is performed by determining the SO2 loss caused by the inlet filter and sample line between the sample manifold and the back of the Model 43S. The following procedure describes the SLIC test:

1. With the Model 43S plumbed for automatic zero, span, and precision checks, generate the span concentration (approximately 90.0 ppb). This procedure is described in Step 8 of this section.
2. After the analyzer is stable, record the reading from **DAS**. Record in the Logbook as S_1.
3. Leave the SO_2 span running and disconnect the calibrator input line in front of the sample filter.
4. Disconnect the Model 43S sample input line on the back of the analyzer and connect the calibrator input line. BE SURE TO EITHER USE THE TEE ON THE SAMPLE LINE TO ALLOW THE TEST GAS TO BE DELIVERED AT AMBIENT PRESSURE.
5. After the analyzer is stable, record the reading from **DAS**. Record in the Logbook as S_2.
6. Calculate the sample line integrity using the following formula:

$$\frac{S_1 - S_2}{S_2} \times 100 = \%\ sample\ line\ integrity$$ [1]

Limits: + / - 2%

7. If the SLIC test is < ±2 percent, reconnect the plumbing in the reverse of Steps 2 through 4.
8. If the SLIC test is > ±2 percent, re-run the test.
9. If the test fails again, check the sample filter and sample line for leaks or dirt. Clean or replace as needed and re-run the test.

If the monitor needs an adjusted calibration (i.e., has been collecting data), it is MANDATORY to perform an UNadjusted calibration prior to performing the adjusted calibration.

1. Before calibrating, record all information requested on the top portion of the SO_2 Calibration Form (Figures 3-1).
2. Initialize **DAS** so that the SO_2 channel is marked DOWN to prevent calibration data from being included in the daily data summary.
3. Adjust the calibrator to deliver zero air to the analyzer by selecting the "CONC Mode" on the Model 9100 and setting the air output to at least 5.0 LPM. The in-station Model 9100 will require no plumbing modifications. If a portable calibrator is used, the SO_2 sample line will need to be plumbed into the output manifold. The VENT port on the output manifold of the portable unit should remain open to allow the Model 43S to sample zero air at atmospheric pressure.
4. Allow at least 10 minutes for the Model 43S to stabilize on the zero air. Observe the stable zero response on **DAS** and record on the SO_2 Calibration Form in the analyzer Logbook.
5. If the zero value is not within ±0.5 ppb, adjust Model 43S zero potentiometer to achieve a zero reading. To turn the potentiometer, release the lock on the potentiometer. Be sure to reset the lock after the adjustment is complete. Wait another five minutes to be sure the instrument is stabile.
6. Assuming the SO2 calibration gas concentration has been programmed into the Model 9100, enter a concentration of 90.0 ppb while in the CONC Mode. If the gas concentration is not programmed into the Model 9100, contact Beth Wittig.

If calculating the concentrations manually, use the following formula:

$$SO_2\ ppm = \frac{Conc_{gas}\ x\ F_{gas}}{F_{air} + F_{gas}}$$

where: $Conc_{gas}$ = span gas cylinder concentration (ppm),
F_{gas} = flow of span gas (sccm), and
F_{air} = flow of the dilution air (sccm).

For example:

$$SO_2\ ppm = \frac{10.0\ x\ 90.0}{10{,}000 + 90.0}$$

$$SO_2\ ppm = 0.0892$$

or

$$SO_2\ ppb = 89.2$$

7. Allow the Model 43S to stabilize for at least 10 minutes. If the instrument response is > +/- 10% of the calculated value, contact Beth Wittig before making any adjustments. To adjust the span response, adjust the span potentiometer until the DAS output agrees with the calculated value. After the analyzer is adjusted, wait for 5 minutes to ensure the analyzer is stabile.
8. Repeat Steps 3 through 5 to be sure the analyzer zero repeats and has not shifted during the adjustments.
9. Repeat Steps 6 and 7 to be sure the span point has not shifted during the zero adjustment.
10. Continue repeating Steps 3 through 5 and Steps 6 and 7 until a value of 0.000 to +/-0.5 ppb is obtained for the zero and a value for the calculated concentration (90.0 ppb) is obtained within ±9.0 ppb of that value without further adjustment of the zero and span potentiometers. Observe the stable zero and span responses on **DAS** and document the results on the SO_2 Calibration Form in the analyzer logbook.
11. *Make no further adjustments to the Model 43S.*
12. In the CONC Mode on the Model 9100, enter 70.0 ppb or calculate the dilution air and span gas flow rates to obtain a span value of approximately 70.0 ppb.
13. If working manually, adjust the ZERO AIR and GAS thumb-wheels to obtain the dilution air and span gas flow rates calculated in Step 12.
14. Allow a minimum of 10 minutes for the Model 43S to stabilize. *Make no adjustments to the Model 43S.* Observe the stable SO_2 response on **DAS**. Document the SO_2 response on the SO_2 Calibration Form in the analyzer logbook.
15. Repeat Steps 12 through 14 for concentrations of 50.0 ppb, 30.0 ppb, and 10.0 ppb. *Make no adjustments to the ZERO BASELINE or SPAN CORRECTION FACTOR..*

[NOTE: For calculation of average percent error and determination of instrument performance, refer to Section 3.2.5.4.]

16. The Field Technician must sign all documents related to the calibration. The calibration must be checked and verified by the Project Manager.

17. Return the Model 9100 to the automatic mode. If a portable calibrator is used, remove the SO_2 sample line from the Model 9100 manifold and reconnect the sample line to the shelter intake manifold. Note the start and stop time of the calibration in the analyzer log book and the station log book. Also note the time the analyzer starts sampling ambient air.

18. Initialize **DAS** so that the SO_2 channel is back on-line to allow ambient SO_2 data to be included in the daily data summary.

4.3 UNADJUSTED CALIBRATION PROCEDURE

[NOTE: Make no adjustment to the SPAN CORRECTION FACTOR or ZERO BASELINE on the Model 43S during this calibration.]

The unadjusted calibration procedures are the same as the adjusted except that no adjustments are made to the instrument prior to the calibration. Refer to section for 3.2.4.2 for the procedures.

4.4 CALCULATION OF SO_2 AVERAGE PERCENT ERROR AND REGRESSION ANALYSIS

1. For each of the SO_2 calibration points, calculate the percent error using the following formula:

$$Percent\ error = \frac{Y_1 - X_1}{X_1} (100)2$$

where: X_1 = known concentration (ppm), and

Y_1 = analyzer response (ppm).

Enter the appropriate values on the SO_2 Calibration Form in the analyzer logbook.

2. Calculate the average SO_2 percent error. If the average of all span points is within ±15 percent of the designated values, the analyzer is in calibration and is responding linearly over the range of interest (0 to 0.500 ppm). If any one point exceeds the 15% error band, another adjusted calibration may have to be performed. Contact Beth Wittig for instructions.

3. Do a least-squares analysis on the data points to determine the slope and intercept of the line that best fits the data. The regression analysis should use the calibrator concentrations as "x" and the corrected instrument response (corrected instrument response = instrument response - zero reading) as the "y". Develop a new calibration

curve for the onsite SO_2 monitor by using results of the comparison to the transfer standard. Record these results on the SO_2 Calibration Form in the analyzer logbook. QA limits for the regression analysis are as follows:

a) Slope (m) $0.85 \geq m \leq 1.15$

b) Intercept (b) < 3 percent of Full Scale

c) Correlation Coefficient (r^2) > 0.995

4. The linear formula used to correct the data according to the regression analysis is:

   $y = mx + b$

   SO_2 monitor (actual) = [SLOPE x SO_2 output] + INTERCEPT.

   The correction formula will be used any time the average instrument response deviation from the actual concentration is $>\pm 10$ percent immediately following an adjusted calibration.

5. AMBIENT SO_2 QA PROCEDURES

The Field Technician should record all activities and results on SO2 service log. Copies of this log including calibration and certification sheets should also be noted in the Station Logbook.

6. CALIBRATION REQUIREMENTS FOR SO_2

The continuous SO2 analyzer will be calibrated during installation and recalibrated whenever any one of the following conditions occurs:

1. Control limit is exceeded for the zero, span, or precision checks;
2. After replacement of major component(s) of an analyzer; and
3. Within 3 months from the last calibration.

A minimum of five calibration points equally spaced over the analyzer range, plus zero, will be used to generate a calibration curve.

SITE SERVICE LOG FOR THERMO ENVIRONMENTAL MODEL 43S SO_2 ANALYZER

Project Name:_____ Project Number:_____

Site:_____ Month:_____ Year:_____

Analyzer Serial Number:_____

SERVICE LOG ITEM	READINGS									
	Week 1		Week 2		Week 3		Week 4		Week 5	
	1	2	1	2	1	2	1	2	1	2
Date										
Range Setting (200 PPB)										
Sample Flow (0.4 – 0.6 LPM)										
Vacuum (-10 to -25 in Hg)										
Time Constant (IN or Out)										
Zero Setting										
Span Setting										
Lamp Voltage (800 - 1200)										
Inlet Filter*										
Operator Initials										
Data Review										
Calibration Tank Pressure (Primary/Secondary)										

*Replace element as needed.

Comments: _____